

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 10/00, 4/60	A1	(11) International Publication Number: WO 97/06186 (43) International Publication Date: 20 February 1997 (20.02.97)
(21) International Application Number: PCT/US96/12989 (22) International Filing Date: 9 August 1996 (09.08.96) (30) Priority Data: 08/513,653 10 August 1995 (10.08.95) US (71) Applicant: ALBEMARLE CORPORATION [US/US]; 451 Florida Street, Baton Rouge, LA 70801-1780 (US). (72) Inventors: LEE, John, Y.; 1524 Stoneliagh Drive, Baton Rouge, LA 70808 (US). DIEFENBACH, Steven, P.; 1457 Bullrush Drive, Baton Rouge, LA 70810 (US). (74) Agents: PIPPENGER, Philip, M. et al.; Albemarle Corporation, 451 Florida Street, Baton Rouge, LA 70801-1780 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR UPGRADING METALLOCENE CATALYSTS (57) Abstract Inorganic and organic impurities are removed from a metallocene catalyst compound comprising the steps of (a) separating inorganic impurities from said compound by forming a solution of said compound in an organic solvent medium which is substantially a non-solvent for said inorganic impurities, (b) treating the solution of said compound with a particulate absorbing material so as to absorb and remove organic impurities from said solution, and (c) separating the solid material, including said particulate absorbing material, from said solution. Optionally, water can be removed by adding a drying agent.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Larvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

PROCESS FOR UPGRADING METALLOCENE CATALYSTS

This invention relates generally to metallocene catalysts which are useful in olefin oligomerization and polymerization and more specifically to an expeditious process for removing impurities which can decrease the efficiency of such catalysts.

5 Metalloenes, when used in combination with co-catalysts such as aluminoxanes, boranes and/or borates are highly active single-site catalysts for olefin polymerization and co-polymerization. The metallocenes can be prepared by reacting a deprotonated ligand, which contains at least one cyclopentadienyl or a related group based on cyclopentadienyl such as indenyl or fluorenyl, with a transition, lanthanide or actinide metal compound, such as a metal halide, or by reacting the ligand with a metal amide. The metallocene product of
10 this metallation reaction may contain both inorganic and organic impurities which, if not removed, can interfere with the activity and efficiency of metallocene when used for single-site catalysis in a gas-phase or slurry phase process. Such purification can involve a number of extraction and recrystallization steps which are time consuming and expensive. We have now found an effective, low cost process for effectively upgrading metallocene catalysts.

15 In accordance with this invention there is provided a process for removing inorganic and organic impurities from a metallocene catalyst compound comprising the steps of (a) separating inorganic impurities from said compound by forming a solution of said compound in an organic solvent medium which is substantially a non-solvent for said inorganic impurities, (b) treating the solution of said compound with a particulate absorbing material
20 so as to absorb and remove organic impurities from said solution, and (c) separating the solid material, including said particulate absorbing material, from said solution. Optionally, water can be removed such as by using a drying agent.

 The resulting solution can be used directly to deposit the purified metallocene on a solid, particulate material to form a supported catalyst such as for use in the gas phase or
25 slurry olefin polymerization process. It can also be used directly as a homogeneous catalyst in a solution polymerization process.

 Metallocene catalyst compounds which can be purified by the process of the invention are organometallic compounds of transition, and especially Group 3, 4, 5 and 6 metals, lanthanide metals and actinide metals. Non-limiting examples of such metals include

Y, Ti, Zr, Hf, V, Ta, Ce, Th, or and Cr. As used herein the term "metallocene" includes derivatives of the metals which contain at least one cyclopentadienyl type moiety. The compounds can be described as metallocene (or bent metallocene in the case of bis-cyclopentadienyl type derivatives) with ancillary anionic ligands or hydrocarbyl groups, such as $Z_t(\eta^5-R'_nH_mC_5)_sMX_{r-s}$, where R' is a carbon or carbon and heteroatom (N, O, S, P, B, or Si) containing group such as C₁ to C₂₀ alkyl, C₃ to C₁₂ cycloalkyl, C₇ to C₂₀ aralkyl or C₆ to C₁₄ aryl. Non-limiting examples of such R' groups include methyl, ethyl, trimethylsilyl, t-butyl, cyclohexyl, phenyl, 4-methylphenyl, 2,4,6-trimethylphenyl, or 2-phenylethyl. The R' substituents can be different in type and in number on each cyclopentadienyl ring and can form fused cyclic groups attached to the rings, such as indenyl, fluorenyl and further substituted derivatives thereof. Z is a bridging group between rings such as silane, phosphine, amine or carbon groups, t is 0 or 1, m and n are integers of 0 to 5, m + n = 5 (or 4 if Z is present), r is 3 or 4, s is 1 or 2 when r = 3 and 1 to 3 when r = 4, M is a transition, lathanide or actinide metal and X is halogen or psuedohalogen (e.g. a leaving group in nucleophilic substitution such as ester, alkoxide, cyanide, tosylate, triflate, or β -diketonate), hydride or C₁ to C₈ alkyl or aryl.

Such metallocenes and other types are described, for example, in U.S. Patent Nos. 2,864,843; 2,983,740; 4,665,046; 4,874,880; 4,892,851; 4,931,417; 4,952,713; 5,017,714; 5,026,798; 5,036,034; 5,064,802; 5,081,231; 5,145,819; 5,162,278; 5,245,019; 5,268,495; 5,276,208; 5,304,523; 5,324,800; 5,329,031; 5,329,033; 5,330,948; 5,347,025; 5,347,026; and 5,347,752, whose teachings with respect to such metallocenes are incorporated herein by reference.

Non-limiting illustrative examples of such metallocenes are bis(cyclopentadienyl)-zirconium dimethyl, bis(cyclopentadienyl)zirconium dichloride, bis(dimethylcyclopentadienyl)zirconium dichloride, bis(methylethyl-cyclopentadienyl)zirconium dichloride, bis(methyl-n-propylcyclopentadienyl)zirconium dichloride, bis(methyl-n-butylcyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)zirconium monomethylmonochloride, bis(cyclopentadienyl)titanium dichloride, bis(cyclopentadienyl)titanium difluoride, cyclopentadienylzirconium tri-(2-ethylhexanoate), bis(cyclopentadienyl)zirconium hydrogen chloride, bis(cyclopentadienyl)hafnium dichloride, racemic and meso dimethylsilanylene-bis(methylcyclopentadienyl)-hafnium dichloride, racemic dimethylsilanylene-bis(indenyl)-

hafnium dichloride, racemic ethylene-bis(indenyl)zirconium dichloride, (η^5 -indenyl)-
 hafnium trichloride, (η^5 -C₅Me₅)-hafnium trichloride, racemic dimethylsilanylene-bis-
 (indenyl)thorium dichloride, racemic dimethylsilanylene-bis(4,7-dimethyl-1-indenyl)-
 zirconium dichloride, racemic dimethylsilanylene-bis(indenyl)uranium dichloride, racemic
 5 dimethylsilanylene-bis(2,3,5-trimethyl-1-cyclopentadienyl)-zirconium dichloride, racemic
 dimethylsilanylene(3-methyl-cyclopentadienyl)hafnium dichloride, racemic dimethyl-
 silanylene-bis(1-(2-methyl-4-ethylindenyl)zirconium dichloride; racemic dimethylsilanylene-
 bis(2-methyl-4,5,6,7-tetrahydro-1-indenyl)- zirconium dichloride, bis(penta-methylcyclo-
 pentadienyl)thorium dichloride, bis(pentamethylcyclopentadienyl)uranium dichloride, (tert-
 10 butylamide)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane titanium dichloride, (tert-
 butylamide)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane chromium dichloride, (tert-
 butylamide)dimethyl(- η^5 -cyclopentadienyl)silane titanium dichloride, (tert-butylamide)-
 dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane methyl titanium bromide, (tert-butylamide)-
 (tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyluranium dichloride, (tert-butylamide)-
 15 tetramethyl- η^5 -cyclopenta-dienyl)-1,2-ethanediyl titanium dichloride, (methyl-amido)-(tetra-
 methyl- η^5 -cyclopentadienyl)-1,2-ethanediyl cerium dichloride, (methylamido)-(tetramethyl-
 η^5 -cyclopentadienyl)-1,2-ethanediyl titanium dichloride, (ethylamido)(tetra-methyl- η^5 -cyclo-
 pentadienyl)methylenetitanium dichloride, (tert-butylamide)-dibenzyl(tetra-methyl- η^5 -cyclo-
 pentadienyl)-silane benzyl vanadium chloride, (benzylamido)dimethyl(indenyl)silane titanium
 20 dichloride, and (phenylphosphido)dimethyl(tetramethyl- η^5 -cyclo-entadienyl)silane benzyl-
 titanium chloride.

The metallocenes can be prepared as known in the art by, for example, reacting the
 appropriate ligand with a deprotonating agent such as an alkali metal, an alkali metal alkyl,
 or a Grignard reagent and then reacting the resulting ligand salt with the transition,
 25 lanthanide or actinide metal compound. Suitable deprotonating agents include, for example,
 Li metal, Na powder, RLi, NaH, LiH, KH or a Grignard reagent (RMgX, where R is C₁ to
 C₁₀ hydrocarbyl and X is halogen). Preferred are alkyllithium compounds such as
 methyllithium, n-butyllithium, s-butyllithium, t-butyl-lithium, or phenyl-lithium.

Usually, the deprotonating agent contained in a hydrocarbon solvent such as hexanes,
 30 cyclohexane, heptane, pentane, or toluene, is added to an acyclic or cyclic ether solution
 of the ligand. Alternatively, the deprotonating agent in hexanes or a mixture of hexanes and

toluene can be added to the dry ligand, with diethyl ether or THF being added, if necessary, to provide a thinner, more workable solution.

The metal compound is usually used in the form of its ether or THF complex; although it can be used directly as a metal halide. The ligand salt need not be recovered
5 from the deprotonation reaction mixture prior to the metallization reaction and can be added to the metal compound or vice versa.

The metal compound such as a metal halide may contain impurities and is usually used in about a 10% stoichiometric excess to provide sufficient metal to react with the deprotonated ligand. These impurities will be carried over into the crude metallocene
10 product. Common impurities in the metal compounds are metal oxides which must be removed because the presence of oxygen in the catalyst can effect its performance as a single-site catalyst. Also, organic impurities, whose presence can be noted by the color of the product, can also effect catalyst performance. The process of the invention effectively and efficiently removes the metal oxide and other inorganic impurities, such as unreacted
15 metal halides, along with the organic impurities from the crude metallocene product. The removal can be carried out in a single vessel.

In the first step of the process the solid product is extracted with a solvent medium so that the solid product dissolves in the solvent medium but the inorganic metal oxides and/or chlorides remain substantially undissolved. The solvent medium, depending upon
20 the solubility of the particular metallocene, can be selected from aliphatic and aromatic hydrocarbon or polar solvents or a combination of such aliphatic, aromatic and/or polar solvents. Non-limiting examples of such solvents include, aliphatic hydrocarbons such as pentane, hexane, heptane, aromatic hydrocarbons and halohydrocarbons such as benzene, chloroform, methylene chloride, toluene, xylenes, and chlorobenzene. In certain cases ether
25 solvents such as diethyl ether can be used.

Sufficient solvent is used to completely dissolve the product without dissolving any substantial portion of the inorganic impurities at the temperature employed which is, preferably, ambient temperatures such that heating or cooling which is required in recrystallization processes is unnecessary. In general, sufficient solvent to produce from
30 about 5 to 50 weight percent solutions of product is used.

Although it is possible to remove the solid inorganic impurities such as by filtration

prior to removal of the organic impurities, this is not necessary because a particulate organic impurity absorbing material can be added to the solution, and then both the solid inorganic impurities and the organic impurity absorbing material can be removed at the same time.

Non-limiting examples of organic impurity removing materials include silica, alumina, silica-alumina, magnesia, zirconia, titania, carbon black, or zeolite. The particle size and porosity are not critical. Preferred, are dried, porous silicas having a water content of 5 percent or less, -OH group contents of from about 0.1 to 3 percent, pore volumes of from about .5 to 3.5 cc/gram and a particle size of from about 30 to 600 microns. The preferred amount of absorbent usually ranges from about 0.1 to 1.0 grams per gram of product to be purified.

The purified solution can be separated from the absorbent and solid inorganic impurities such as by filtration. For example, the solution can be poured into a glass column which has a coarse frit plate and the product containing filtrate recovered. The solid filter cake can be washed with additional solution to recover additional product. In another embodiment, the solution can be passed into the absorbent which is supported in a short column to begin with. In either case, the solution can be recycled through the column one or more times so as to remove additional organic impurities.

The product metallocene can be recovered by removal of the solvent or the solution can be used directly to form a supported catalyst, such as for use in the gas phase or slurry polymerization process. It can also be used as a homogeneous catalyst in the solution polymerization process. The metallocene can be deposited from the solution onto a catalyst support before or after reacting the metallocene with a co-catalyst such as an aluminoxane, a borane, a borate or a mixture thereof. Any water which is introduced into the metallocene solution by the purification process can be removed by drying techniques such as by passing the solution through activated molecular sieves.

The invention is further illustrated by, but is not intended to be limited to, the following examples.

Example 1

Crude bis(1-n-butyl-3-methylcyclopentadienyl)-zirconium dichloride (5.3 grams) which contains about 3 weight percent inorganic zirconium chloride/oxide impurities is

- 6 -

placed in a vessel and sufficient heptane is added with stirring to give 25.0 grams (~ 21%) of solution and the mixture is stirred at 22°C for 0.5 hour to precipitate inorganic impurities. Dried silica (Davidson 952, 3.0 percent OH group by LOI, 1 gram) is added to the solution at 22°C to absorb organic impurities and stirred for just less than one minute; the silica becomes dark brown in color and the n-heptane solution changes from an original brown color to yellow/orange. The mixture is filtered through a glass column equipped with a coarse-frit plate to remove the solid inorganic impurities and the colored silica. The filtration is repeated twice by passing the solvent back through the column such that the heptane solution becomes pale yellow. The filter cake is rinsed twice with heptane (2 x 12.5 g.) And a total of 47.34 grams of solvent is collected. The heptane is removed (50°C/27 in Hg vacuum) to give 4.68 g. (88 percent recovery) of pure bis(1-n-butyl-3-methylcyclopentadienyl)zirconium dichloride. Toluene is added to give a 25 weight percent solution; proton NMR shows that it contains a trace of water. In the heptane solution the water does not hydrolyze the product to form oxo impurities i.e. the metallocene is stable under the process conditions used. About 0.5 g. of activated 4A molecular sieves is added to remove the water (2 hours). Proton NMR shows that the pale yellow toluene solution contains 25.0 weight percent pure metallocene product.

Example 2

Bis(n-butylcyclopentadienyl)zirconium dichloride (1.0 gram, light-tan color, mp 96-98°C, 96% pure) is dissolved at 22°C with stirring in a solvent mixture of pentane (6.0 grams) and methylene chloride (4.0 grams). This cloudy, yellow-orange solution is filtered through a glass funnel equipped with a coarse-frit plate to remove the solid impurities. The orange, wet cake is rinsed twice with the same pentane/methylene chloride solvent (2 x 2.0 grams) and about 14 grams of yellow solution is collected (in which there is 0.94 gram of metallocene product). Dried silica (Davidson 952, 3.0 percent OH group by LOI, 0.37 gram) is added with stirring at 22°C into the metallocene solution to absorb organic impurities. Just within one minute, the silica becomes yellow in color and the pentane/ methylene chloride solution changes from an original yellow color to water-clear. Again the mixture is filtered through a glass funnel equipped with a coarse-frit plate to remove the colored silica. The filter cake is rinsed once with 4.0 grams of pentane/methylene chloride solvent

- 7 -

and a total of about 16 grams of solution is collected. The solvent is removed at 10-22°C/20-27 in Hg vacuum to give 0.87 gram of snow-white bis(n-butylcyclopentadienyl)zirconium dichloride (mp 98-100°C, 99% pure).

What Is Claimed Is:

1. A process for removing inorganic and organic impurities from a metallocene catalyst compound comprising the steps of (a) separating inorganic impurities from said compound by forming a solution of said compound in an organic solvent medium which is substantially a non-solvent for said inorganic impurities, (b) treating the solution of said compound with a particulate absorbing material so as to absorb and remove organic impurities from said solution, and (c) separating the solid material, including said particulate absorbing material, from said solution.
2. The process of claim 1 wherein said particulate absorbing material is an porous inorganic oxide.
3. The process of claim 2 wherein said porous inorganic oxide is silica.
4. The process of claim 1 wherein the absorbing material and the inorganic impurities are simultaneously separated from said solution by filtration.
5. The process of claim 4 wherein the filtrate is recycled through the filter cake.
6. The process of claim 1 wherein, after the solid material has been removed from the solution, the solution is contacted with a solid, particulate material so as to deposit the metallocene on said material.
7. The process of claim 1 including the step of removing water from said solution.
8. The process of claim 7 wherein the water is removed by adding a drying agent to the solution.
9. The process of claim 1 wherein said metallocene is a Group 4 metal compound.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/12989

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/60

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	POLYMER BULLETIN, vol. 35, no. 1/02, 1 July 1995, pages 87-94, XP000507166 RIEGER B ET AL: "ETHYLENE-BRIDGED ANSA-ZIRCONOCENE DICHLORIDES FOR SYNDIOSPECIFIC PROPENE POLYMERIZATION" see page 89, paragraph 2	1-4,9
X	EP,A,0 500 944 (MITSUI) 2 September 1992 see page 19; example 23	1,4,6,9
X	WO,A,92 05203 (EXXON) 2 April 1992 see page 30, line 11 - line 17; examples A,PART4 see page 31, line 16 - line 24; examples B,PART4	1-4,9
A	see examples 1,3	6

	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

14 October 1996

Date of mailing of the international search report

11. 11. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Fischer, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/12989

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 026 798 (CANICH JO ANN M.) 25 June 1991 see page 18; examples A,PART4 ---	1-4,9
X	EP,A,0 495 099 (MITSUI) 22 July 1992 see page 18; example 3 -----	1-3,9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/12989

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-500944	02-09-92	WO-A- 9201723 KR-B- 9409020 CA-A- 2066247	06-02-92 29-09-94 25-01-92
WO-A-9205203	02-04-92	US-A- 5057475 AT-T- 132507 AU-B- 656498 AU-A- 8651891 CA-A- 2090972 DE-D- 69116157 DE-T- 69116157 EP-A- 0548257 ES-T- 2082233 JP-T- 6501037 US-A- 5227440	15-10-91 15-01-96 02-02-95 15-04-92 14-03-92 15-02-96 02-05-96 30-06-93 16-03-96 27-01-94 13-07-93
US-A-5026798	25-06-91	AU-B- 667292 AU-A- 8754291 EP-A- 0548277 JP-T- 6505033 WO-A- 9205204 US-A- 5420217 US-A- 5504169 AT-T- 141275 AU-A- 6248390 AU-B- 643237 AU-A- 6443990 CA-A- 2024899 CA-A- 2065745 DE-D- 69028057 DE-T- 420436 DE-T- 662484 EP-A- 0420436 EP-A- 0491842 EP-A- 0662484 EP-A- 0671404 EP-A- 0643066 ES-T- 2079332 JP-A- 3188092 NO-B- 178891	21-03-96 15-04-92 30-06-93 09-06-94 02-04-92 30-05-95 02-04-96 15-08-96 21-03-91 11-11-93 18-04-91 14-03-91 14-03-91 19-09-96 15-02-96 27-06-96 03-04-91 01-07-92 12-07-95 13-09-95 15-03-95 16-01-96 16-08-91 18-03-96

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/12989

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5026798		NO-B- 178895	18-03-96
		NO-A- 953466	14-03-91
		WO-A- 9104257	04-04-91
		US-A- 5547675	20-08-96
		US-A- 5055438	08-10-91
		US-A- 5057475	15-10-91
		US-A- 5168111	01-12-92
		US-A- 5227440	13-07-93
		US-A- 5264405	23-11-93

EP-A-495099	22-07-92	JP-A- 2173014	04-07-90
		JP-A- 2173016	04-07-90
		JP-A- 2173015	04-07-90
		CA-A, C 2008315	24-07-90
		EP-A- 0685498	06-12-95
		EP-A- 0685496	06-12-95
		WO-A- 9007526	12-07-90
		JP-A- 2276807	13-11-90
		US-A- 5525689	11-06-96
		US-A- 5218071	08-06-93
		US-A- 5336746	09-08-94
